# MECHANISTIC CONSIDERATIONS IN RETROGRADE REACTION

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INTRODUCTION

The importance of retrogressive reactions has become obvious through the study of liquefaction kinetics and products, but the fundamental chemical reactions and their kinetics have remained more obscure. For instance, researchers such as Neavel recognized some time ago that soluble products could be generated *and consumed* very rapidly under coal liquefaction conditions.[1] Similar observations have been made for pyridine solubles under pyrolysis conditions, where there is no added solvent [2]. In a sense the whole technology of heavy oil conversion is bound up with retrograde reactions, in that thermal treatment of petroleum asphaltenes under a variety of conditions can produce similar amounts of distillate, but the amount of retrograde product (coke) generated in conjunction with these volatiles is critically dependent on conditions of catalyst, medium, and hydrogen pressure.[3,4] Thus the impact of retrograde processes has been quite obvious, but the detailed nature of the responsible bond forming reactions has remained unclear.

Similarly, hydrogen transfer has been acknowledged for many years to play a key role in coal liquefaction, though not until more recently was it recognized as a prerequisite to the cleavage of strong bonds in both liquefaction and pryolysis.[5,6] The extension of the induced strong-bond scission picture and the consideration of its microscopic reverse provides new insights for bond-forming processes. Thus, the reverse of H-atom displacement of C-C or O-C linkages to aromatic clusters is the addition of a C-centered or O-centered radical *to* an aromatic ring system, to displace an H-atom. When the adding radical is resonance stabilized, the addition is highly reversible. Just as the key step in the de-substitution (cleavage) reaction is H-atom transfer to the coal linkage, the key step in the microscopic reverse (the substitution reaction) is H-atom transfer *from* the substitution adduct.
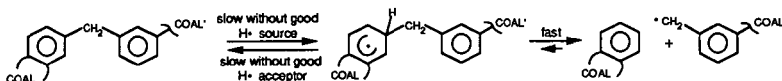
In this paper we extend some earlier qualitative discussion[7] of these aspects of bond formation with the quantitative results of a numerical model. This model was originally assembled to fit and help interpret experimental data for bond cleavage in model systems;[8] however, since it includes the reverse of essentially all of the fundamental reaction steps incorporated, it is equally suitable for exploring bond formation, or retrograde reaction. We use it here to illustrate limits on the ability to scavenge radicals, the relative importance of recombination and addition, and the key role of H-atom removal from retrograde intermediates.

MODELING CONSIDERATIONS AND PROCEDURES

Chemical Constituents. We chose the addition of stabilized radicals, as indicated in Scheme 1 above, as the major retrograde reaction type on which to focus, not because we believe it to necessarily be always the most important class of retrograde reaction, but as a highly reversible reaction, its outcome is quite sensitive to changing hydrogen-transfer conditions. However, since for completeness the model necessarily incorporates the possibility of recombination of resonance stabilized radicals, that route to retrograde products is also examined. Retrograde reaction by recombination of course also depends on H-transfer to "lock in" a stable product, since otherwise the weak bond formed by recombination will not represent a permanent retrograde linkage.

The mechanistic numerical model we have used incorporates a single surrogate "coal" structure [1,2-(1,1'-dinaphthy)lethane] in a reaction medium consisting of aromatic/hydroaromatic mixture (phenanthrene/dihydrophenanthrene) of various compositions, with and without H_2 overpressure. This four starting-component reaction system provides for both weak-bond- and strong-bond scission, H-transfer by H-atom abstraction, free H-atom addition, reverse radical-disproportionation, and RHT, retrograde reaction by radical addition, radical recombination, and radical displacement. When limited to only the more important reactions, including virtually all of the reverse reactions, this provides a set of more than 40 species and 150 reactions. Thus the model is very detailed in that it that incorporates all relevant fundamental chemical reactions (non-ionic) of essentially all species, both closed shell and free radical, in the reaction system. Because of this mechanistic detail, the model, of necessity, is very simple in that it includes only a very limited set of starting structures. To limit the complexity, we have confined the model to a pure hydrocarbon system, though the same general considerations will also apply to systems containing phenolics, where the presence of the -OH groups will in all likelihood further promote radical addition (as well as promoting attack of electrophilic fragments and the subsequent loss of hydrogen as a proton).

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Mechanistic Considerations. The model is homogeneous; it consists of relatively low-molecular-weight species assumed to be miscible in all proportions. We have made the simplifying assumptions that the system is free of concentration gradients and requires no mass- or heat-transport.* The activity of H_2 in solution is taken to equal that provided by presumed equilibrium with the gas-phase H_2 pressure.

We emphasize that this model was *not* intended in any way to actually simulate the conversion of a real coal, or even, in the present case, to match exactly the experimental retrograde behavior of model systems, but to provide a general illustration of how chemical factors influence certain classes of retrograde reactions under different circumstances. However, because the strength of the weak central bond in 1,2-dinaphthylethane (55 kcal/mol) leads to a 400°C-half-life of about 12 minutes at 400°C, it was previously chosen by other researchers[9] as a prototypical linkage type that would give coal linkages lifetimes similar to those observed for actual coals during liquefaction, *assuming* the dominant bond cleavage reaction is weak-bond scission. We subsequently subjected a polymeric version of 1,2-dinaphthylethane to donor solvent liquefaction conditions, and observed a product mixture that strikingly revealed some of the shortcomings of the then-accepted weak-bond scission picture of coal liquefaction.[10] As it happens, the numerical modeling results presented here reproduce some of the experimental observations on bond scission, notwithstanding the fact that nothing has been done to force such a correspondence, except to use the best available experimental or estimated rate parameters for each of the individual reactions included in the numerical model. We therefore expect the model to provide valid illustrations, in general terms, of the relative importance of retrograde reaction types under various circumstances.**

As reflected by the total number of reactions, the scheme that follows from even the limited set of starting structures used here appears rather complex, but is based on relatively few reaction types. These reaction types and the products in which they result are shown below in Scheme 2. In the figures that follow, we generally have grouped together all of a common product that follows from several different examples of a given reaction type, and have identified them by a generic heading, rather than individual acronyms used in the integration program.

Scheme 1. Categories of Bond Cleavage and Bond Formation

"Strong-bond cleavage-1"

This category includes all H-atom displacements, or hydrogenolyses, from 1,2-dinaphthylethane (producing naphthalene and ethylnaphthalene), from all sources of H-atoms: free H•, RRD, and RHT, coming from either solvent or substrate species.

"Strong bond cleavage-2"

This category also generates ethylnaphthalene, but results instead from displacement (i.e., addition-elimination) by radical species other than H-atom. "Strong-bond cleavage-2" is not a *net* cleavage, in that whenever the displacing radical is a naphthylmethyl radical, one aryl-aryl coupling is simply being traded for another.

"True retrograde product"

In the present work, dinaphthylmethane is the dominant coupling product that, as indicated above, is companion to the cleavage product generated in strong-bond cleavage-2. This coupling product is formed from attack of a naphthylmethl radical on the starting substrate 1,2-dinaphthylethane, or on the other products naphthylmethane or naphthyl ethane. It is also formed in a "net" retrograde reaction by addition of naphthylmethyl radical to naphthalene, followed by successful removal of the ipso hydrogen from the initial adduct. The term "true retrograde product" is used here because the bond is about 87 kcal/mol, with a homolytic half-life of more than 10 years even at 500°C.

"Weak bond cleavage"

The "weak-bond cleavage" product is of course the naphthylmethane that results from scavenging of the naphthylmethyl radicals that are generated by homolysis of the weak (ca. 55 kcal/mol) central bond in dinaphthylethane.

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* Limits on miscibility are of course very important in retrograde reactions, as evidenced by the importance of micelle formation during coke formation in heavy-oil upgrading. However, covalent bond formation is both a *cause* of, and a *result* of, phase separation. Therefore it is probably not possible to find a simple partisan answer to the question of which of these most controls coke formation and other retrograde processes.

** Since this model was originally used with a more limited set of reactions to address the competition in cleavage processes between H-transfer by free H-atoms, the reverse of radical-disproportionation (RRD), and radical hydrogen-transfer (RHT), and since the outcome of such attempts at deconvolution of parallel, competing H-transfer processes is still a matter of dispute, it is reasonable to ask whether that dispute should cast doubt on the illustrations and conclusions provided below. The answer to this question is no. Just as the functional form of overall cleavage dependence does not allow one to easily assign exact proportions of the transferred H to free H•, RRD, and RHT, when they are in competition, so also any error that may exist in the assigned parameters for RHT will not result in any gross miss-statement of bond formation outcomes that we are addressing here.

"Recombination product "

The "recombination product" is simply the dinaphthylmethane that results from recombination of the initial weak-bond scission product, naphthylmethyl radical. In reality it is indistinguishable from the starting material itself, but in the numerical integration simulations is distinguished by nomenclature from the original molecules of the starting material. The recombination product undergoes all of the reactions that the original starting material does. Since this recombination product is itself just as fragile as the starting material, in the area graphs that follow, the amount of the recombination product that survives is so small that it cannot be seen on the scale of the figures.

"Stilbene product"

The fragility of the recombination product of course does not apply to the "stilbene product," which is the naphthalene analog of stilbene resulting from loss by various processes of 2(H) from either the original dinaphthylethane substrate or the recombination product that comes from the reversal of the weak-bond cleavage. The central double bond of this stilbene analog is very strong, and represents one of the ways that weakly bonded recombination products can be converted to more refractory retrograde products.*

Integration Procedure. The conversion simulations using this model were performed on a VAX 11/750 computer using a numerical integration routine based on the Gear algorithm. Some of the results are shown below using area graphs to depict the evolution of various products as a function of time, or bar graphs to show product distributions at a fixed time for different starting compositions. The time-steps used in the integration were very much smaller than the time steps output by the program and used to construct the area graphs shown here.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the computed product distribution for the "bibenzylic" starting material in a system of minimal H-donor content . There is of course rapid loss of substrate, but not all to desired products: about 2/3 of the mass after 2 hours, consists of uncleaved or retrograde products. The recombination product itself is not visible on the scale of the figure: it has either re-homolyzed, or lost 2(H) to form the "stilbene" product. The weak-bond cleavage product is substantial, but accounts for slightly less than 15% of the mass of starting material. The two strong-bond cleavage products (displacement by H• and by R•) are almost as prominent as the weak-bond cleavage product, even though the original donor content of the system was quite low (ca. 15 m% of substrate). In an actual coal, the stilbene retrograde product would not persist, owing to the thermodynamic driving force for unsaturation to be grouped in aromatic systems.

For comparison, Figure 2 shows the effects of added H_2 at 400°C. Strong-bond cleavage product 1 (displacement by free H• *and* solvent-mediated H•) has increased about five-fold, and is now more important than strong-bond cleavage product 2, which has actually declined. Weak-bond cleavage product has increased substantially, and the stilbene product has declined. Interestingly, the "true retrograde" product (dinaphthylmethane from H• and R• displacement reactions) has increased substantially, so that the sum of stilbene and true retrograde product is essentially unchanged by the addition of H_2. The important observation here is that while the presence of 1000 psi H_2 has markedly increased the strong-bond cleavage that results from displacement by H•, there has been essentially *no* suppression of the true retrograde products. That is, H_2 in a purely thermal system clearly does indeed react with resonance stabilized radicals in the system (as Vernon showed experimentally some years ago[11]) to substantially increase strong-bond cleavage, but the "scavenging" aspect of this reaction has essentially no effect retrograde reaction by addition-elimination reactions of resonance-stabilized radicals. Clearly, there is a large increase in H-atom activity, but no significant fractional decrease in resonance-stabilized radical concentration.

The result of the inability to fully scavenge stabilized radicals, is that at long reaction times such radicals will continue to form retrograde products through addition-elimination reactions, particularly in the present case, through displacement of methyl radical from the weak-bond cleavage product, methylnaphthalene. The consequence of this factor is that long reaction times or higher temperatures tend to be beneficial *only* in the presence of H_2 or a H-donor, as illustrated in Figure 3, which shows the sum of cleavage products with and without H_2 at several different sets time/temperature conditions.

Comparisons of the effectiveness of two different H-donors, dihydrophenanthrene and 9,10-dihydroanthracene leads to additional interesting observations of short-term vs long-term behavior. At short reaction times, where there is a large generation of fragment radicals from homolysis of the weakly bonded coal surrogate, modeling indicates that dihydroanthracene, as the better scavenger, indeed maximizes the yield of capped fragment radicals, and minimizes the yield of recombination products and radical displacement retrograde products.

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* Although the double bond in stilbene is "very strong," this refers to the enthalpy input required to break the double bond directly, forming two naphthylcarbene moeities. As a non-aromatic double bond, there will be a great tendency for any stilbene-like double bond to undergo rearrangements such that all unsaturation comes to reside in aromatic structures. Such "tertiary" reactions are not included in the present model.

However, at long reaction times, the "better" scavenger actually *enhances* the yield of retrograde product. This is because, at longer reaction times when the burst of radicals from the decomposing coal has largely died away, the principal source of fragment radicals is abstraction of hydrogen atoms from the previously capped fragment species by the pool of scavenger radicals generated by the scavenger itself. Thus, the model appears to further explain a trend which has been noted previously, namely that coal conversion tends to be better in the presence of hydroaromatics that are **not** the best scavengers, and is evidently better because these latter scavengers tend to be better hydrogenolysis reagents, while being poorer radical initiators.

The origin of the effects of H_2 can be seen more clearly with the help of Figures 4 and 5. Figure 4 shows that hydrogen pressure (at a somewhat higher temperature where they occur more strongly in these uncatalyzed systems) serves, as expected, to partially maintain the H-donor (dihydrophenanthrene) level in the reaction medium. Figure 5 shows that the percent increase in hydrogenolysis rates is much higher than the percent increase in donor concentration. In other words, the total new H-atom activity resulting from the presence of H_2 is much larger than the increase in H-donor. Thus, in the short term, the steady-state concentration of H· and ArH· has increased more than the steady-state concentration of ArH_2.

Returning to the observation that scavenging increases hydrogenolysis, but does not, through its "scavenging" action, decrease the rate of formation of retrograde products, Figure 6 shows the computed ratios of scavenger concentration ($[H_2]/[PhenH_2]$), the ratios of scavenging by these two components, and the percent of recombination that occurs (for $H_2 = 0$ and 1000 psi.) for the naphthylmethyl radicals produced by homolysis of the original weak bond. Clearly, not only is the scavenging ability of H_2 inconsequential, compared even to a small concentration of H-donor (as expected because of their greatly different bond strengths), but the ability of H_2 to limit recombination is barely observable, even at 600°C.

Perhaps more surprising are the computed effects of H_2 or added H-donor on stabilization of the "true retrograde" intermediate (the removal of H-atom from the ipso-substituted radical addition intermediate). Figure 7 shows the instantaneous net rate of stabilization at by each of the major H-transfer processes for three different starting conditions: no added H_2 and 0.1 M $PhenH_2$, 1000 psi H_2 and 0.1 M $Phen_2$, and 0 H_2 and 0.5 M $PhenH_2$. In all three cases, H-removal by radical disproportionation with 9-hydrophenanthryl- naphthylmethyl- and dinaphthylethyl-ethyl radicals gives a net formation rate for the dinaphthylmethane retrograde product. Either added H_2 or increased starting H-donor actually serve to *increase* the net rate of formation of the true retrograde product by radical addition and H-atom removal in disproportionation processes. This increased formation by the first three categories is more than compensated for by large negative rates of retrograde product formation by free H-atoms and RHT. That is, free H-atoms transfer much more H to dinaphthylmethane than they take away from ipso-H-substituted dinaphthylmethane, and are net destroyers, not net formers, of retrograde product. Thus, addition of H_2 or H-donor does *not* actually prevent retrograde product formation (it in fact increases it), but serves to cleave such products more effectively *after* they are formed!

This finding makes somewhat moot earlier discussions of whether coal linkages are dominated by strong or by weak bonds: Even if coal starts out with many of most of its linkages connected by weak bonds, there will very shortly be many strong bonds formed, whose subsequent cleavage will likely by critical to the ultimate conversion yield from the coal. The findings here also serve to articulate and explain our earlier experimental observations with a polymeric version of the dinaphthylethane substrate[10] we have computationally studied here: even when a substrate has a weak bond between every pair of asromatic clusters, as in 1,2-diarylethane linkages, there will be much cleavage not only of the weak bond between the two aliphatic carbons in the linkage but also of the strong aryl-alkyl bonds at either side. This cleavage will result not only from hydrogenolysis, but also from displacement by carbon-centered radicals to form retrograde products with new, strong linkages that can only be cleaved by hydrogenolysis. Thus in many cases, coal liquefaction may be as much about cleaving retrograde bonds as it is about cleaving linkages that are original to the coal structure.

SUMMARY AND CONCLUSIONS

In some cases the results presented here are a quantitative illustration of what can be qualitatively anticipated from thermochemical considerations, while in other cases the results were qualitatively surprising. The major conclusions and points to be emphasized from the modeling results are the following.

- All scavengers that operate via a radical capping process have a dual role—they also act as initiators.

- Higher temperatures provide more reaction, but if there is not something to mitigate retrograde reactions, higher temperatures tend to cause the retrograde reactions to increase as fast or faster than the bond-cleavage reactions. This modeling result appears to be completely in accord with the common observation that increasing liquefaction temperature beyond about 440°C tends to lower coal conversion, and similarly in pyrolysis, that higher heating rates tend

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to decrease char yields, *primarily* when the higher heating rates are associated with more rapid removal of volatile products.

- The presence of H_2 does *not* inhibit retrograde product formation as much as it hydrogenolyzes retrograde products faster after they are formed. In fact, modeling indicates that H_2 can, at certain reactions times, *increase* the yield of retrograde products.

- The impact of added H_2 on hydrogenolysis (at least in the short term) does *not* come primarily through its maintenance of a useful hydroaromatic content, as has often been postulated in coal liquefaction, but through a higher steady state concentration of H• that is established long before the hydroaromatic content can be substantially affected.

ACKNOWLEDGMENT

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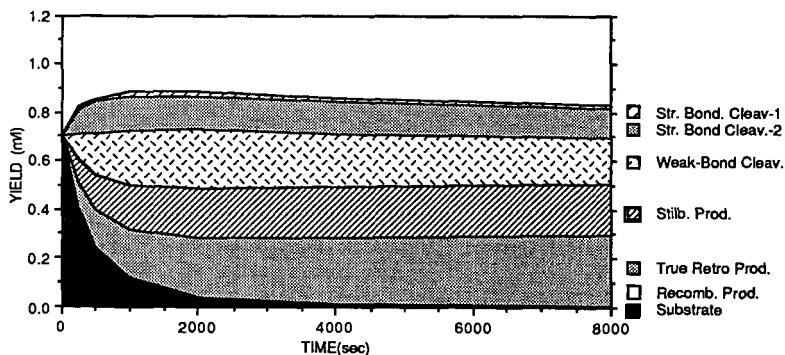11. Vernon, L. W. *Fuel*, **1980**, *59*, 102.

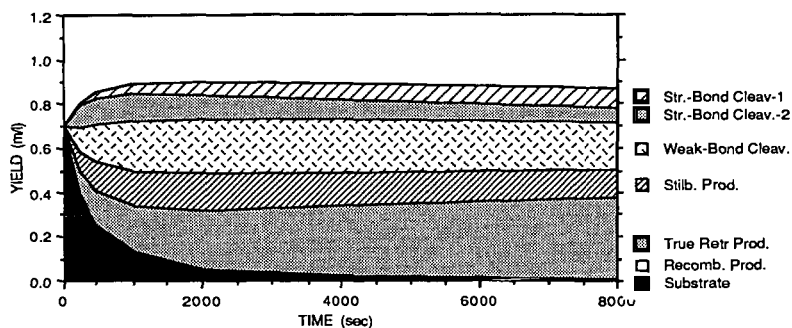Figure 1. Computed product distribution at 400°C with minimal H-donor content. [PhenH2] = 0.1M, P (H2) = 0.

Figure 2. Computed product distribtuion at 400°C with minimal donor content but added H_2. [PhenH$_2$] = 0.1M, P (H_2) = 1000 psi.
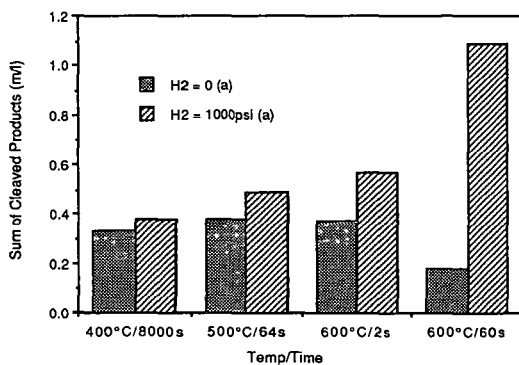

Figure 3. Sum of cleavage products for different time and temperature conditions. [PhenH$_2$] = 0.1M.
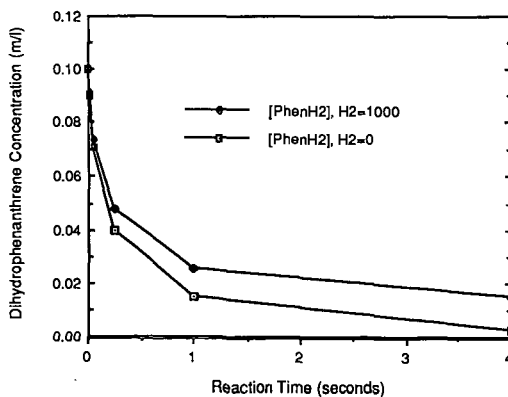

Figure 4. Computed H-donor concentration at 500°C as a function of time with and without 1000 psi added H_2. [PhenH$_2$] = 0.1M.
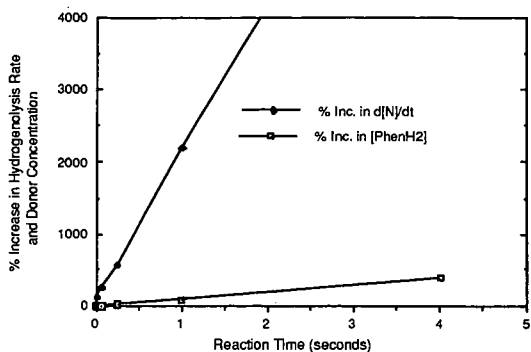
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Figure 5. Comparison of percent increase in hydrogenolysis rate and donor concentration as a result of 1000 psi added H_2. 500°C; [PhenH2] = 0.1M.
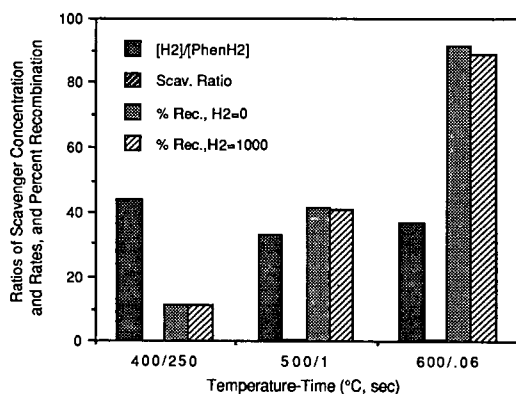

Figure 6. Computed ratios of scavenger concentration, scavenging rates for H_2 and H-donor, and the percent recombination of homolysis fragments with and without 1000 psi H_2. [PhenH2] = 0.1 M.
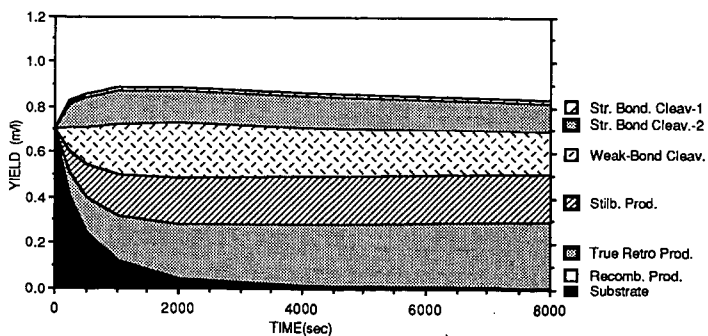

Figure 7. Computed net rates of H-removal from diarylmethane retrograde intermediate for various H-tran

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